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(57) Abstract

Catalytic composition which can be used in the Fischer-Tropsch process essentially consisting of an inert carrier, cobalt in a quantity ranging from 1 to 50 % by weight, preferably from 5 to 35 % by weight, and tantalum in a quantity ranging from 0.05 % to 5 % by weight, preferably from 0.1 to 3 % by weight.

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CATALYTIC COMPOSITION SUITABLE FOR THE FISCHER-TROPSCH

PROCESS

The present invention relates to a catalytic

composition suitable for the preparation reaction of

5   hydrocarbons by means of the so-called Fischer-Tropsch

synthesis; it also relates to the catalytic process for

the preparation of hydrocarbons for which it is used.

More specifically, the present invention relates

to a new catalytic composition for the production of

10   hydrocarbons by means of the Fischer-Tropsch synthesis

containing Cobalt and promoted by Tantalum, this

composition being obtained by reacting derivatives of

the above elements in the presence of a suitable

carrier, as specified in more detail hereunder.

15   The selection of cobalt as main constituent of the

active phase is due to the fact that this favours the

formation of saturated linear hydrocarbons with a high

molecular weight minimizing the formation of oxygenated

and olefinic compounds, contrary to the well-known

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catalytic systems based on iron.

The known art cites numerous examples of catalysts based on cobalt used for the synthesis of paraffinic products with various distributions.

5   Since the first works of Fischer in 1932 (H.H Storch, N. Golumbic, R.B. Anderson, "The Fischer Tropsch and Related Synthesis", John Wiley & son, Inc., New York, 1951) - which described the development of a $Co/ThO_2/MgO$ system supported on kieselguhr - until

10   today, the patented systems based on cobalt are essentially the following: $Co/Mg/ThO_2$ supported on kieselguhr (1954, Reinpruessen A.G.), Co/MgO supported on bentonite (1958, M.W. Kellog), Co/Th/Mg (1959, Rurchemie), Co/Th supported on silica-gel (1960, Esso Res.& Eng.),

15   Co/Mg/Zr/Kieselguhr (1968, SU-A-660.324, Zelinskii INST.), Co/Ru/Keiselguhr (1976, US-A-4.088.671 GULF), $Co/Zr/SiO_2$ (1980, GB-A-2.073.237, Shell), Co/Ru supported on titanium (1988, US-A-4.738.948 Exxon), Co/Re/REO,K supported on alumina (1988, EP-A-313.375,

20   Statoil), $Co/Mo,W/K,Na/SiO_2$ (1991, GB-A-2.258.414, IFP), $Co/Ru/Cu/K,Sr/SiO_2$ (1993, EP-A-581.619, IFP).

The effect of promoters on the system based on cobalt, from what is described in literature, is multiple; however it can be subdivided into various groups

25   in relation to the function of the promoter (B. Jager,

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R. Espinoza in Catalysis Today 23, 1995, 21-22).

For example, promoters such as K, Na, Mg, Sr, Cu, Mo, W and metals of group VIII essentially increase the activity. Ru, Zr, rare-earth oxides (REO), Ti increase

5 the selectivity to hydrocarbons with a high molecular weight. Ru, REO, Re, Hf, Ce, U, Th favour the regenerability of the catalyst.

Among the various promoters, ruthenium, alone or together with other elements, is certainly the most

10 widely used.

The recent evolution of catalytic systems for the synthesis of hydrocarbons has led to the idenfitication of various promoters to be coupled with cobalt in order to increase both the activity of these systems in terms

15 of conversion of the reagents and also the selectivity to linear hydrocarbons with a high molecular weight. This evolution has taken place mainly in the last twenty years. The increase in price of crude oil in the 70s' provided the incentive for exploring other ways of

20 producing liquid fuels and chemicals, among which the possibility of transforming synthesis gases into hydrocarbon products with a high molecular weight by means of the Fischer-Tropsch synthesis.

As far as the Fischer-Tropsch synthesis is con-

25 cerned, this can refer to the hydrogenation process of

carbon monoxide to produce higher hydrocarbons and

oxygenated molecules with a prevalently linear chain.

The reaction takes place in the presence of a mixture

of hydrogen and carbon monoxide with or without carbon

5   dioxide (so-called synthesis gas) at temperatures lower

than 350°C and at pressures of between 1 and 100 atm.

The wide range of catalysts and their modifica-

tions described in the known art and the wide range of

operating conditions for the reduction reaction of

10   carbon monoxide with hydrogen allows a considerable

flexibility in the selectivity of the products, ranging

from methane to heavy waxes with alcohols and olefins

as by-products. The distribution of the products can be

explained by the known growth mechanism obtained by a

15   polymerization kinetics and processed by Anderson

Shultz and Flory (P. Biloen, W.M.H. Sachtler, Advance

in Catalysis, Vol. 30, pages 169-171, Academic Press,

New York, 1981; R.B. Anderson, Catalysis, Vol. IV, P.H.

Emmett ed., Reinhold, New York, 1956). In accordance

20   with this model, the attempt to restrict the range of

products in order to maximize for example the C_5-C_{11}

fraction (gasoline-range) results in selectivities to

methane and the C_2-C_4 fraction of more than 40%. In

addition the products obtained are essentially paraf-

25   fins with a linear chain and olefins with a low octane

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number. The only possibility of deviating from the nature imposed by the Fischer-Tropsch polymerization kinetics is to identify catalytic systems which do not adhere to this kinetics mechanism. Typical examples are
5 systems developed by Mobil which substantially couple the properties of the Fischer-Tropsch catalysts with the shape selectivity of zeolites (US-A-4.157.338).

The possibility of maximizing the selectivity to heavy liquids and waxes (essentially paraffinic and
10 without sulfur) offers on the other hand various advantages. In particular it is possible to minimize the selectivity to methane and the gas fraction. The subsequent treatment (e.g. hydrocracking, hydroiso-merization) of this liquid-solid fraction of a paraf-
15 finic nature gives high quality medium distillates if compared with the medium distillates obtained from petroleum (Ball J., Gas. Matters, April 27 1989, pages 1-8). In this context the typical characteristic of catalysts based on cobalt to be highly selective in the
20 production of higher paraffins is definitely advanta-geous. In addition, the use of catalysts with a reduced water gas shift activity, such as catalysts based on cobalt, implies a low selectivity to CO_2, contrary to the use of a traditional catalyst based on iron.

25   With respect to the productivity of catalysts

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based on cobalt, defined as weight of C_{2+} hydrocarbons/weight of catalyst/time, from what is specified in literature, this seems to vary a great deal and to depend directly on the operating temperature. Increas-

5 ing the operating temperature however is not a valid way of increasing the productivity to high quality liquid and solid hydrocarbons, as this would cause a consequent increase in the selectivity to methane and light gases. It is very important on the contrary from

10 an economical point of view to maximize this productivity and to minimize at the same time the selectivity to methane. In other words it is important to maximize the production of high quality liquid and solid hydrocarbons (C_{9+}, C_{22+}).

15   In accordance with this important objective, it is necessary for the catalyst to be capable of combining a high productivity (Prod.C_{2+}) with a low selectivity to methane (Sel.CH_4).

         A catalytic composition has now been found which,

20 applied to the Fischer-Tropsch process, enables a high selectivity to C_{2+} hydrocarbons and at the same time a low selectivity to methane.

         In accordance with this, the present invention relates to a catalytic composition based on cobalt

25 which allows conversions of the mixture of CO and H_2,

known as synthesis gas, with or without N_2 and/or CO_2 and/or light gases (C_1-C_4), into saturated linear hydrocarbons containing from 77% to 88% by weight of C_{5+} and from 24 to 31% by weight of C_{9+} and with productivi-

5 ties into C_{2+} of between 180 and 330 $gC_{2+}/Kg_{cat}/h$, maintaining a low selectivity to methane.

The catalytic composition of the present invention essentially consists of an inert carrier, cobalt in a quantity of from 1 to 50% by weight, preferably from 5

10 to 35% by weight, and tantalum in a quantity of from 0.05 to 5% by weight, preferably from 0.1 to 3% by weight, the complement to 100 consisting of the inert carrier, the cobalt and tantalum being present in metal form or in the form of a derivative.

15 The percentages of cobalt and tantalum are expressed as metals.

The cobalt and tantalum can be present as metal or as derivatives, in the latter case the oxide form being preferred.

20 As far as the inert carrier is concerned, this is preferably selected from at least one of the oxides of at least one of the following elements: silicon, aluminum, zinc, magnesium, titanium, zirconium, yttrium, tin and the relative mixtures.

25 The inert carrier which can be used is independent

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of the crystallographic structure of the above oxides.

For example, aluminas can be used of any phase compo-

sition such as η, γ, δ, θ, α and the relative mixtures.

In the same way, when the inert carrier essential-

5 ly consists of TiO_2, this can be in the form of rutile

and/or anatase.

In the preferred embodiment, the inert carrier is

selected from silica, γ alumina, δ alumina, titania and

the relative mixtures, even more preferably from

10 silica, γ alumina and the relative mixtures.

A further object of the present invention relates

to a process for the preparation of the catalytic

composition of the present invention which comprises:

a)   a first deposition onto the inert carrier, prefer-

15 ably selected from silica and alumina, preferably via

dry impregnation, of a cobalt salt; subsequent calcina-

tion to give a catalytic precursor; subsequent optional

reduction and passivation of the calcined product;

b)   deposition onto the catalytic precursor thus

20 obtained of a derivative of tantalum, preferably via

wet impregnation; subsequent calcination, optionally

followed by reduction and passivation.

The cobalt and tantalum can be deposited according

to various methods well known to experts in the field

25 such as, for example, ion exchange, dry impregnation,

wet impregnation; precipitation and coprecipitation,
gelation and mechanical mixing.

In the case of cobalt however, the dry impregna-
tion method is preferable. According to this technique,
5 the material to be impregnated is put in contact with
a volume of solution more or less equal to the pore
volume. In step (a) it is preferable to use aqueous
solutions of cobalt salts, such as halides, nitrate,
oxalate, the complex formed with lactic acid and
10 lactates, the complex formed with tartaric acid and
tartrates, the complex formed with acetylacetonates. In
the most preferred embodiment, cobalt nitrate is used.

In the case of tantalum on the other hand, this is
preferably deposited by means of any impregnation
15 technique, preferably wet impregnation. According to
this technique, the inert carrier onto which the cobalt
has been previously deposited, is completely covered
with a solution of a derivative of tantalum, particu-
larly tantalum alcoholates, such as ethoxide, propoxi-
20 de, isopropoxide, methoxide. In the most preferred
embodiment tantalum ethoxide dissolved in C_1-C_5 alcohols
is used.

The inert carrier can be used partially or totally
in the first phase. In the latter case all of the inert
25 carrier is used in the preparation of the catalytic

precursor in the first step. In the former case the inert carrier is used partially in the first step and partially in the second step.

In the preferred embodiment, the process of the
5 present invention comprises the above steps a) and b) without the reduction and passivation phases.

As far as the calcination is concerned, this is a heating step at a temperature of between 400°C and 750°C to remove volatile substances and decompose the
10 derivatives of cobalt and tantalum into oxides. The calcination is carried out in the presence of oxygen, air or other gases containing oxygen.

Before this step, the material can be subjected to drying, usually at reduced pressure at a temperature of
15 between 80 and 120°C, with or without an inert gas. This operation has the purpose of eliminating (or strongly reducing) the possible solvents or water with which the material has been impregnated and gives dispersion homogeneity to the active phase.

20   With respect to the reduction, this is a step in which the material is treated with a reducing agent, preferably hydrogen or gas containing hydrogen. The reduction is carried out at a temperature of between about 250°C and about 500°C, preferably from 300° to
25 450°C for periods of time of between 0.5 and 24 hours,

at pressures between atmospheric pressure and 40 bars.

As far as the passivation is concerned, this is carried out by treating the material with oxygen diluted with an inert gas, usually nitrogen. The

5 temperature is preferably from 10 to 80°C. Using for example nitrogen containing 1-2% of oxygen with a stream of 2 litres/hour/$g_{cat.}$, the passivation step can have a duration of from 1 to 5 hours at 25°C.

Some of the operating details relating to the

10 preparation of the above catalytic compositions will however be more evident on reading the experimental examples below which, however, do not limit the catalytic compositions of the present invention.

A further object of the present invention relates

15 to a process for the preparation of essentially linear, saturated hydrocarbons starting from synthesis gas (Fischer-Tropsch process) in the presence of the above catalytic composition.

The conversion of the synthesis gas into hydrocar-

20 bons takes place at a pressure normally between 1 and 100 bars, preferably from 10 to 75 bars, at a temperature generally within the range of 150°C to 350°C, preferably from 170°C to 300°C, even more preferably from 200°C to 240°C. The hourly volumetric flow-rate is

25 generally from 100 to 20000, preferably from 400 to

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5000, volumes of synthesis gas per volume of catalyst
and per hour. The ratio H_2/CO in the synthesis gas is
generally from 1:2 to 5:1, preferably from 1.2:1 to
2.5:1. Other gases, particularly CO_2 may also be
5 present.

As is known to experts in the field, the prepara-
tion of the mixture of CO and H_2 can be carried out
starting from natural gas prevalently consisting of
methane. The oxidating agent can be oxygen or air. In
10 the latter case it is evident that the mixture of
synthesis gas will also contain a considerable quantity
of nitrogen, which may or may not be eliminated of CO/H_2
before the Fischer-Tropsch reaction. The advantage of
carrying out the Fischer-Tropsch reaction on mixtures
15 in which nitrogen is still present, is evident.

The catalyst can be used in the form of fine
powder (about 10-700 mm) or in the form of particles
having an equivalent diameter of from 0.7 to 10 mm,
respectively in the presence of a liquid phase (under
20 the operating conditions) and a gaseous phase, or a
gaseous phase. The liquid phase can consist of at least
one hydrocarbon having at least 5, preferably at least
15, carbon atoms per molecule. In the preferred embodi-
ment, the liquid phase essentially consists of the same
25 reaction product.

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Just to give an example, the catalysts of the present invention can be used in a fixed-bed reactor, fed in continuous with a mixture of CO and H_2 and operating under the following conditions:

5 - reaction temperature: 200-240°C

   - reaction pressure: 20 bars

   - space velocity (GHSV):   500-1500 h^{-1}

   - H_2/CO mixture: 2/1

The reaction temperature is regulated in order to 10 obtain a conversion higher than at least 45% of the volume of carbon monoxide fed (conv. CO%).

Following these conditions, the catalysts prepared as described in examples 1 to 11 were evaluated, using various carriers. The compositions are summarized in 15 table 1.

The results of the reactivity tests are indicated in tables 2 to 4.

Catalysts supported on SiO_2

Comparative example 1.

20 <u>Comparative catalyst A</u>

(Co/Ru/SiO_2; 14% Co, 0.2% Ru).

A silica carrier (having a surface area of 520 m^2/g, a specific pore volume of 0.8 m^3/g, an average particle diameter of 0.5 mm, a specific weight of 0.42 25 g/ml) is dry impregnated with a nitric solution of

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$Co(NO_3)_2 \cdot 6H_2O$ at pH = 2.5 in such quantities as to obtain a percentage of Co equal to 14% by weight referring to the total. The silica thus impregnated is dried at 120°C for 16 hours, calcined at 400°C in air

5 for 4 hours, then treated in a stream of H_2 at a space velocity (GHSV) of 1000 h^{-1}, in a tubular reactor at 400°C for 16 hours. The sample thus reduced is passivated in a mixture of $(1\%)O_2/(99\%)N_2$ with GHSV of 1000 h^{-1} for 2 hours at room temperature.

10 A 7.5 10^{-3} M solution is added to the monometallic sample, of $Ru(NO_3)_3 \cdot xH_2O$ obtained with the following procedure: precipitation in the form of hydroxide at pH = 7.2 of $RuCl_3 \cdot xH_2O$, subsequent elimination of the chlorides, resolubilization in conc. HNO_3 and dilution

15 in CH_3COCH_3 in a ratio 1:250 v/v.

The acetone solution of ruthenium is added to the sample in such a quantity as to have 0.2% of Ru by weight referring to the total. The slurry is left under stirring for 2 hours and then dried under vacuum

20 < 10mmHg at 50°C. A calcination phase in air follows at 350°C for 4 hours and subsequently a reduction and passivation analogous to that described above.

Comparative example 2.

Comparative catalyst B

25 $(Co/Sc/SiO_2;$ 14% Co, 0.2% Sc).

For the preparation of catalyst B, a solution of $Sc(NO_3)_2$ 10^{-3} M in acetone is added to 50 g of the monometallic catalyst Co/SiO_2 prepared as described in example 1, in such a volume as to obtain a final weight

5   percentage of Sc equal to 0.2%.

The suspension thus obtained is left under stirring for two hours and is then dried under vacuum at 50°C. The sample is calcined at 350°C for 4 hours in air, reduced at 400°C in H_2 for 16 hours with a GHSV of

10   1000 h^{-1} and passivated in (1%)O_2/(99%)N_2 with a GHSV of 1000 h^{-1} for 2 hours at room temperature.

Example 3. Catalyst C1

($Co/Ta/SiO_2$; 14% Co, 0.5% Ta).

A solution of $Ta(EtO)_5$ 0.01 M in ethanol is added

15   to 50 g of the monometallic catalyst Co/SiO_2 prepared as described in example 1, in such a volume as to obtain a final weight percentage of tantalum equal to 0.5%.

The suspension thus obtained is left under stir-

20   ring for two hours and is then dried under vacuum at 50°C.

The sample is calcined at 350°C for 4 hours in air, reduced at 400°C in H_2 for 16 hours with a GHSV of 1000 h^{-1} and passivated in (1%)O_2/(99%)N_2 with a GHSV of

25   1000 h^{-1} for 2 hours at room temperature.

Example 3b. Catalyst C2

$(Co/Ta/SiO_2;$ 14% Co, 0.2% Ta).

The catalyst C2 is prepared analogously to what is described in example 3.

5 **Example 4.** Catalyst D

$(Co/Ta/SiO_2;$ 14% Co, 0.5% Ta).

A silica carrier (having a surface area of 520 m^2/g, a specific pore volume of 0.8 m^3/g, an average particle diameter of 0.5 mm, a specific weight of 0.42

10 g/ml) is dry impregnated with a nitric solution of $Co(NO_3)_2 \cdot 6H_2O$ at pH = 2.5 in such quantities as to obtain a percentage of Co equal to 14% by weight referring to the total. The silica thus impregnated is dried at 120°C for 16 hours and calcined at 400°C in

15 air for 4 hours. A solution of $Ta(EtO)_5$ 0.01 M in ethanol is added to the monometallic sample Co/SiO_2 in such a volume as to obtain a final weight percentage of tantalum equal to 0.5%.

The suspension thus obtained is left under stir-

20 ring for two hours and is then dried under vacuum at 50°C.

A calcination phase in air follows at 350°C for 4 hours.

Catalyst supported on TiO_2

25 **Comparative example 5.** Comparative catalyst E

$(Co/Ru/TiO_2;$ 12% Co, 0.2% Ru).

Following the procedure described in example 1, comparative catalyst E is prepared completely similar to catalyst A but having TiO_2 as carrier instead of

5 SiO_2. In this case the TiO_2 had a surface area of 25 m^2/g, a specific pore volume of 0.31 cm^3/g and a content of rutile equal to 81%.

Comparative example 6. Comparative catalyst F

$(Co/Sc/TiO_2;$ 12% Co, 0.2% Sc)

10   Catalyst F is prepared analogously to what is described for the preparation of catalyst B.

Example 7. Catalyst G

$(Co/Ta/TiO_2;$ 12% Co, 0.5% Ta).

Following the procedure described in example 4,

15 catalyst G is prepared, consisting of the carrier based on titania. In this case the TiO_2 had a surface area of 25 m^2/g, a specific pore volume of 0.31 cm^3/g and a content of rutile equal to 81%.

Catalysts supported on SiO_2-TiO_2

20 **Example 8. Catalyst H**

$(Co/Ta/[Si-Ti];$ 15% Co, 0.5% Ta).

A silica carrier (having a surface area of 480 m^2/g, a specific pore volume of 0.8 m^3/g, a particle size of between 75 and 150 μm, a specific weight of

25 0.55 g/ml, average pore radius of 35 Å) previously

dried at 150°C for 8 hours is suspended, under a nitrogen atmosphere, in anhydrified n-hexane, 6 ml/g SiO_2. A solution of $Ti(i-PrO)_4$ 0.2 M is added to the slurry in such a quantity as to have about 7.0% of Ti;

5 the mixture is left under stirring for 16 hours and is then dried under vacuum with a pressure of <10 mmHg and a temperature of 50°C. The sample thus obtained is calcined in a nitrogen atmosphere at 400°C for 4 hours and subsequently calcined in air at 600°C for a further

10 4 hours.

Catalyst H is prepared with the mixed carrier thus obtained, consisting of 7.1% of titanium of which about 25% in crystalline form (50% rutile, 50% anatase) and a surface area of 440 m^2/g, analogously to what is

15 described in example 4.

Catalysts supported on Al_2O_3

Example 9. Catalyst I

($Co/Ta/Al_2O_3$; 14% Co, 0.5% Ta).

Catalyst I is prepared analogously to what is

20 described in example 4, with an alumina carrier (crystalline phase 100% gamma, surface area of 175 m^2/g, specific pore volume 0.5 m^3/g, average pore radius 40 Å, particle size between 20-150 μm, specific weight of 0.86 g/ml).

25 **Example 10.** Catalyst L

(Co/Ta/Al$_2$O$_3$; 12% Co, 0.5% Ta).

Catalyst L is prepared analogously to what is described in example 4, with an alumina carrier (crystalline phase 50% γ and 50% δ, surface area of 137 m^2/g, specific pore volume 0.46 m^3/g, average pore radius 45 Å, particle size between 20-120 μm, specific weight of 0.69 g/ml).

CATALYTIC TESTS

Example 11. Evaluation of the catalytic activity of catalysts supported on silica.

The catalyst (A, B, C, D according to examples 1-4) is formed in particles having a diameter of between 0.35 and 0.85 mm and is subsequently diluted with an inert carrier, silicon carbide, having the same particle size as the catalyst and in a volumetric ratio catalyst/inert carrier equal to 1:2. The catalyst thus diluted is then charged into a tubular reactor and subjected to an activation procedure in a stream of hydrogen (2000 Nl/h·l$_{cat}$) and nitrogen (1000 Nl/h·l$_{cat}$), at a temperature of between 350-400°C and a pressure of 1 bar for 16 hours. The temperature is then lowered to 180°C, the volumetric flow-rate of hydrogen and nitrogen is modified (333-1000 Nl/h·l$_{cat}$) and (5000-15000 Nl/h·l$_{cat}$) respectively, the system is pressurized to 20 bars and carbon monoxide is then introducted (116.5-500

Nl/h·l$_{cat}$) to obtain a volumetric ratio H$_2$/CO equal to 2.

The flow-rate of nitrogen in the starting phase of
the reaction is progressively lowered until complete
elimination according to the following sequence (the
5   lower flow-rates refer to tests with GHSV = 500h^{-1}, the
higher flow-rates to GHSV = 1500 h^{-1}):

time	flow-rate H$_2$	flow-rate CO	flow-rate N$_2$
(hrs)	(Nl/h·l$_{cat}$)	(Nl/h·l$_{cat}$)	(Nl/h·l$_{cat}$)
0	333-1000	166.5-500	5000-15000
1	333-1000	166.5-500	3750-11250
2	333-1000	166.5-500	2500-7500
3	333-1000	166.5-500	1250-3750
4	333-1000	166.5-500	0

At the end of the starting phase, the reaction
15 temperature is regulated so as to obtain a conversion
of carbon monoxide with respect to the volume fed
(conv. CO%) of less than 20% for at least 48 hours,
then in the following 48 hours the temperature is
gradually increased until a minimum CO conversion value
20 of 45% is reached, without however exceeding the reac-
tion temperature of 240°C, in order to minimize the
production of methane as well as the light gaseous
fractions (C$_2$-C$_4$).

As indicated in table 2 for comparative catalyst
25 A, in order to reach conversions of CO higher than the

limit of 45%, it is necessary to increase the reaction

temperature (from 200°C to 240°C) with an increase in

the volumetric flow-rates of the mixture H_2-CO (GHSV

from $500h^{-1}$ to $1500h^{-1}$). As a result the selectivity to

5 methane is favoured (from 7.8% to 29.7%), expressed as

percentage referring to the total carbon present in the

products (C%), to the total disadvantage of the selec-

tivities to higher hydrocarbons (Sel.C_{22+} from 15.4% to

3.2%, Sel.C_{9+} from 66.9% to 48.8%), expressed as per-

10 centage referring to the total weight of the whole

hydrocarbon fraction produced (weight %).

With respect to comparative catalyst B, promoted

with scandium, using a total volumetric flow-rate equal

to $1500h^{-1}$ and a reaction temperature of 218°C, an

15 hourly weight productivity to hydrocarbons with more

than two carbon atoms (C_{2+}) equal to 273 g/kg/h and

selectivities to C_{22+} of 14.2% are obtained. In general

the catalytic performances of catalyst B can be consid-

ered as being higher than those of catalyst A.

20 Catalysts C1, C2 and D of the present invention,

containing Tantalum, are subjected to an analogous

catalytic test. As indicated in table 2, with a total

volume flow-rate (GHSV) equal to $1500h^{-1}$ and a reaction

temperature of 220°C, for catalysts C1 and C2, prepared

25 with the same procedure as catalysts A and B, CO

- 22 -

conversions are obtained of 60.3% and 69.3% respectively, productivities to C_{2+} of more than 315 $gC_{2+}/Kg_{cat}/h$, selectivities to methane of less than 10%, selectivities to C_{22+} higher hydrocarbons of about 24%,

5   selectivities to C_{9+} hydrocarbons of between 65.6% and 71.3% and finally selectivities to C_{5+} of more than 81%.

These performances are better than those obtained with comparative catalysts A and B, especially for the higher productivities, selectivities to higher hydro-

10 carbons and lower selectivities to methane and light gas fractions (C_2-C_4).

With respect to catalyst D, synthesized with the procedure described in example 4, the catalytic performances of the Co/Ta system are further improved com-

15 pared to the comparative catalysts: CO conversions of 71.0%, productivities to C_{2+} of 330 $gC_{2+}/Kg_{cat}/h$, selectivities to methane of 8.4%, selectivities to C_{22+} higher hydrocarbons of 29.1%, selectivities to C_{9+} hydrocarbons of 78.4% and finally selectivities to C_{5+}

20 of 83.5%.

Example 12. Evaluation of the catalytic activity of catalysts supported on Titania

As indicated in table 3, also in this case the comparison between the reference catalysts promoted

25 with ruthenium (cat. E) or scandium (cat. F) and the

catalyst promoted without the intermediate reduction

and passivation phase (example 3), shows an increase in

the CO conversion, total hydrocarbon productivity and

selectivity to higher hydrocarbons, maintaining a low

5   selectivity to methane (CO conv. = 70.0%, Prod.C_{2+} = 172

g/Kg_{cat}/h, C_{22+} = 32.9%, CH_4 = 7.6%).

Example 13. Evaluation of the catalytic activity of

catalysts supported on silica/titania and alumina.

The catalytic composition Co/Ta supported on other

10 materials such as the mixed carrier silica-titania and

alumina with a different phasic composition showed

interesting catalytic performances at reaction tempera-

tures of between 209 and 218°C and total volumetric

flow-rates of 1500 h^{-1}.

15   As indicated in table 4, the conversions obtained

are higher than 57% (CO conv. = 65.8÷57.1%), producti-

vities to C_{2+} higher than 180 g/kg/h (Prod.C_{2+} :

183.1÷260.1 g/kg/h), selectivities to hydrocarbons C_{22+}

higher than 23% (Sel.C_{22+}: 23.2÷28.3).

20   The data of table 5 show the possibility of using

synthesis gas diluted with nitrogen.

Table 1

	Example	Cat.	%Co	%X	X	Carrier
	Comp.1	A	14	0.2	Ru	SiO_2
5	Comp.2	B	14	0.2	Sc	SiO_2
	3	C1	14	0.5	Ta	SiO_2
	3b	C2	14	0.2	Ta	SiO_2
	4	D	14	0.5	Ta	SiO_2
	Comp.5	E	12	0.2	Ru	TiO_2
10	Comp.6	F	12	0:2	Sc	TiO_2
	7	G	12	0.5	Ta	TiO_2
	8	H	12	0.5	Ta	SiO_2-TiO_2
	9	I	14	0.5	Ta	$\gamma-Al_2O_3$
	10	L	12	0.5	Ta	$\gamma,\delta-Al_2O_3$

15

Table 2

===

Example 11

Catalysts supported on Silica

Catalyst	A	A	A	B
React. temp.(°C)	200	220	240	218
GHSV h^{-1}	500	1.000	1.500	1.500
CO conv. (%)	48.5	51.3	47.1	57.6
Prod.C_{2+} (g/Kg/h)	81.4	149	183.5	272.6
CH_4 (C%)	7.8	18.8	29.7	10.3
CO_2 (C%)	0.3	1.8	2.2	0.1
C_1-C_4 (wt%)	13.5	32.7	49	17.3
C_{22+} (wt%)	15.4	14.1	3.2	14.2
C_{9+} (wt%)	66.9	64.1	48.8	-
C_{5+} (wt%)	86.5	67.3	51	82.8

===

Tabl 2 cont.

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Example 11

Catalysts supported on Silica

5	Catalyst	C1	C2	D
	React. temp.(°C)	212	222	220
	GHSV h^{-1}	1.500	1.500	1.500
	CO conv. (%)	60.3	69.3	71
	Prod.C_{2+} (g/Kg/h)	315.3	326.2	330.1
10				
	CH_4(C%)	7.1	9.5	8.4
	CO_2 (C%)	0.9	0.5	0.6
	C_1-C_4 (wt%)	15.9	19	16.5
	C_{22+} (wt%)	23.9	24.7	29.1
15	C_{9+} (wt%)	65.6	71.3	78.4
	C_{5+} (wt%)	84.1	81.1	83.5

===

Table 3

Example 12

Catalysts supported on Titania

Catalyst	E	F	G
React. temp.($^\circ$C)	228	228	214
GHSV h^{-1}	1.500	1.500	1.500
CO conv. (%)	54.3	61.6	70
Prod.C_{2+} (g/Kg/h)	144.6	152.3	171.7
CH_4(C%)	7.6	13.3	7.6
CO_2 (C%)	0.1	0.1	0.1
C_1-C_4 (wt%)	12.6	19	12.1
C_{22+} (wt%)	21.9	17.6	32.9
C_{5+} (wt%)	87.4	81	87.9

Table 4. Catalysts supported on Si-Ti and alumina

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Example 13

Catalysts supported on Si-Ti and alumina

Catalyst	H	I	L
React. temp.($^{\circ}$C)	209	214	218
GHSV h^{-1}	1.500	1.500	1.500
CO conv. (%)	65.8	59	57.1
Prod.C_{2+} (g/Kg/h)	260.1	183.1	196.2
CH_4(C%)	10.5	9.8	8.5
CO_2 (C%)	0.4	0.5	0.5
C_1-C_4 (wt%)	19.4	22.4	17.6
C_{22+} (wt%)	23.2	28.3	24.8
C_{9+} (wt%)	68.2	65.5	70.4
C_{5+} (wt%)	80.6	77.6	82.4

==

Table 5

Test in the presence of Nitrogen		
5 Catalyst	I	I
React. temp.($^{\circ}$C)	226	235
GHSV h^{-1}	1.500	1.500
Content & N_2	20.6	20.6
CO conv. (%)	44	65.4
10 Prod.C_{2+} (g/Kg/h)	120.4	173.5
CH_4(C%)	15	13.4
CO_2 (C%)	0.4	0.9
C_1-C_4 (wt%)	27	28
15 C_{22+} (wt%)	28.2	21.4
C_{9+} (wt%)	59.1	62.6
C_{5+} (wt%)	73	72

CLAIMS

1.   A catalytic composition essentially consisting of
     an inert carrier, cobalt in a quantity of from 1
     to 50% by weight, and tantalum in a quantity of
5   from 0.05 to 5% by weight,
     the complement to 100 consisting of the inert
     carrier;
     the cobalt and tantalum being present in metal
     form or in the form of a derivative.

10 2.   The catalytic composition according to claim 1,
     characterized in that the cobalt is present in a
     quantity of from 5 to 35% by weight and the
     tantalum from 0.1 to 3% by weight.

3.   The catalytic composition according to claim 1,
15   characterized in that the inert carrier is select-
     ed from at least one of the oxides of at least one
     of the following elements: silicon, aluminum,
     zinc, magnesium, titanium, zirconium, yttrium, tin
     and the relative mixtures.

20 4.   The catalytic composition according to claim 1,
     characterized in that the inert carrier is select-
     ed from silica, γ alumina, δ alumina, titania and
     the relative mixtures.

5.   The catalytic composition according to claim 4,
25   characterized in that the inert carrier is select-

ed from silica, γ-alumina and the relative mix-
tures.

6. A process for the preparation of the catalytic
compostion according to claim 1 which comprises:

5   a) a first deposition onto the inert carrier,
preferably selected from silica and alumina, of a
cobalt salt; subsequent calcination to give a
catalytic precursor; subsequent optional reduction
and passivation of the calcined product;

10   b) deposition onto the catalytic precursor thus
obtained of a derivative of tantalum; subsequent
calcination, optionally followed by reduction and
passivation.

7. The process according to claim 6, characterized in
15   that the cobalt is deposited onto the inert
carrier following the dry impregnation technique.

8. The process according to claim 6, characterized in
that the tantalum is deposited via wet impregna-
tion.

20 9. A process for the synthesis of essentially linear
and saturated hydrocarbons starting from synthesis
gas basically consisting of CO and H_2, possibly
diluted with nitrogen, comprising reacting this
mixture in the presence of the catalyst according
25   to claim 1, at a pressure of between 1 and 100

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   B01J23/847   C07C1/04   B01J23/755

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   B01J   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 328 158 A (INNES ROBERT A ET AL) 4 May 1982	
A	US 5 559 065 A (LAUTH GUENTER ET AL) 24 September 1996	
A	US 4 206 135 A (KUGLER EDWIN L ET AL) 3 June 1980	
A	US 4 738 948 A (FIATO ROCCO A ET AL) 19 April 1988 cited in the application	
A	US 4 088 671 A (KOBYLINSKI THADDEUS P) 9 May 1978 cited in the application	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 October 1998	09/11/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Thion, M

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US 5559065	A	24-09-1996	DE 4221011 A		05-01-1994
			DE 59305516 D		03-04-1997
			EP 0576944 A		05-01-1994
US 4206135	A	03-06-1980	NONE		
US 4738948	A	19-04-1988	EP 0319625 A		14-06-1989
			AU 595967 B		12-04-1990
			AU 8250787 A		15-06-1989
			US 4822824 A		18-04-1989
US 4088671	A	09-05-1978	NONE		

bars, a temperature of between 150°C and 350°C, the molar ratio H_2/CO in the synthesis gas being from 1:2 to 5:1.

10. The process according to claim 9, characterized in that the reaction temperature is between 170°C and 300°C, the pressure between 10 and 75 bars, the ratio H_2/CO in the synthesis gas being from 1.2:1 to 2.5:1.

11. The process according to claim 10, characterized in that the temperature is from 200°C to 240°C.